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Field scale variability of solute transport parameters and related soil properties

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Abstract

The spatial variability of transport parameters has to be taken into account for a reliable assessment of solute behaviour in natural field soils. Two field sites were studied by collecting 24 and 36 small undisturbed soil columns at an uniform grid of 15 m spacing. Displacement experiments were conducted in these columns with bromide traced water under unsaturated steady state transport conditions. Measured breakthrough curves (BTCs) were evaluated with the simple convective-dispersive equation (CDE). The solute mobility index (MI) calculated as the ratio of measured to fitted pore water velocity and the dispersion coefficient (D) were used to classify bromide breakthrough behaviour. Experimental BTCs were classified into two groups: type I curves expressed classical solute behaviour while type II curves were characterised by the occurrence of a bromide concentration maximum before 0.35 pore volumes of effluent ($MI < 0.35$) resulting from preferential flow conditions. Six columns from site A and 8 from site B were identified as preferential. Frequency distributions of the transport parameters (MI and D) of both sites were either extremely skewed or bimodal. Log-transformation did not lead to a normal distribution in any case. Contour maps of bromide mass flux at certain time steps indicated the clustering of preferential flow regions at both sites. Differences in the extent of preferential flow between sites seemed to be governed by soil structure. Linear cross correlations among transport parameters and independently measured soil properties revealed relations between solute mobility and volumetric soil water content at time of sampling, texture and organic carbon content. The volumetric field soil water content, a simple measure characterising the soil hydraulic behaviour at the sampling location, was found to be a highly sensitive parameter with respect to solute mobility and preferential flow situations. Almost no relation was found between solute transport parameters and independently determined soil properties when non-preferential and preferential samples were considered separately in regression analyses. Future work should concentrate to relate integrated parameters such as the infiltration rate or the soil hydraulic functions to solute mobility under different flow situations.

Introduction

There is overwhelming evidence that spatial variability plays an important role in solute transport through natural soils. Comprehensive field studies have been carried out using techniques such as suction soil solution samplers (Butters *et al.*, 1989; Roth *et al.*, 1991; Van Weesenbeck and Kachanoski, 1991), soil columns (Jury *et al.*, 1986; Ward *et al.*, 1995), or soil coring (Ellsworth *et al.*, 1991) to elucidate the effect of soil heterogeneity on transport phenomena at the field scale. The underlying aim of these studies was to define the random space function of the pertinent solute transport parameters and so to estimate, for instance, the range of solute travel times at a certain soil depth. In broader context, such studies aim to improve the understanding of solute transport mechanisms operating at the field scale and their governing soil intrinsic and extrinsic factors. Butters *et al.* (1989) monitored bromide concentrations following a pulse application in a 0.64 ha field

using vacuum solution samplers at seven depths and 16 locations and averaged these concentrations to characterise the field scale solute movement. The extremes in local bromide breakthrough revealed a bimodal travel time distribution at every soil depth. The movement of chloride was studied with a large number of suction cups at single and multiple depths along a longitudinal transect by Wesenbeeck and Kachanoski (1991) and Roth *et al.* (1991) respectively. The pattern of solute movement was observed to be quite irregular, with unexpected fast (preferential) flow occurring in part of the soil volume, and slower flow in the remainder.

Examination of soil columns collected from a regular grid is less tedious than the suction cup approach to account for the inherent field scale water and solute transport variability. Jury *et al.* (1986) examined 36 undisturbed soil columns and attributed the faster of the double peak breakthrough behaviour of a reactive tracer to preferential

flow. Recently Sassner *et al.* (1994) also found from leaching tests of chloride in 29 large undisturbed soil monoliths (20 cm in diameter and 1 m long, sampled at irregular grid in about 0.3 ha field) that the distribution of the specific discharge of water was characterised by two distinct populations quantified adequately by a bimodal distribution. Ellsworth *et al.* (1991) derived resident concentration data from soil coring, a third approach to assess variability in solute flux in a field experiment. In contrast to the aforementioned studies, additional soil physical properties at various locations in the experimental field were also determined to supplement the information on solute (chloride) breakthrough. Data on the independently measured soil bulk density and gravimetric soil water content were used in a piston flow model to predict solute movement in the vadose zone. Values computed were in good agreement with the measured centre of mass of the chloride pulse. This result suggested that solute transport might be predicted directly from more easily measurable soil properties. But many uncertainties about field scale solute movement and its relation to other soil properties still remain, in particular for situations involving preferential flow.

However, the extent to which bimodal distributions of water and or solute transport parameters are related to soil properties like bulk density, water content, texture, organic carbon or saturated hydraulic conductivity is unclear. Nor is it known if simple empirical equations could be derived to predict solute mobility at the field scale using independently measured soil parameters as was done for soil hydraulic properties (pedo-transfer functions, Rawls and Brakensiek, 1985). To answer some of these questions, the soil column approach was preferred to determine the space function of solute mobility because it allows adjustment of flow conditions at both ends of the soil volume and thereby minimises the uncertainties arising from the flow regime. Based on the hypothesis that a larger number of (even small) columns will sample the heterogeneity in a field better than a small number of large columns, relatively small columns (5.7 cm in diameter and 10 cm long) were used in our apparatus, similar to that described by Rambow and Lennartz (1993). Thus, bromide displacement studies were conducted under unsaturated steady state water flow conditions in 24 and 36 undisturbed soil columns collected from two sites in northern Germany. At both sites, the soil columns were collected at a uniform grid spacing of 15 m, which, though large, was selected to evaluate the impact of variability on solute transport in small sized agricultural fields with a limited number of samples. Attempts were made to isolate the columns with preferential flow features and evaluate their contribution in the field scale solute distribution pattern. Saturated hydraulic conductivity, gravimetric soil water content, bulk density, soil texture, and organic carbon content were determined independently for every sampling location and correlations were calculated between

these properties and solute movement parameters with the broad objective to identify the properties which may potentially contribute towards the preferential flow phenomenon.

Material and Methods

SAMPLING AND DETERMINATION OF SOIL PROPERTIES

Both experimental sites were situated in Northern Germany in the vicinity of the city of Kiel. Site A was cropped with spruces; no tillage had occurred in the 5 years prior to sampling. Conversely, site B was subjected to conventional agro-practices and received a mould-board ploughing once a year. Sampling was performed in late autumn. Soil type of site A was sandy loam with a crumb structure, while site B had loamy soil with subangular structure. The soils were classified according to FAO standards as mollic Cambisol (site A) and as dystric Gleysol (site B). Sampling locations at both sites were chosen at 15 m grid spacing resulting in sampled area of 45 m × 75 m at site A (24 columns) and 45 m × 120 m at site B (36 columns). The field sampling started by carefully removing the surface soil layer (5 cm) at each location and collecting undisturbed soil columns for leaching experiments by slowly pushing and pounding sharp edged steel cylinders (5.7 cm in diameter and 10 cm long) vertically into the soil. Adjacent to each core, a second undisturbed soil column (5.7 cm in diameter and 5 cm long) was taken for saturated hydraulic conductivity (K_{sat}) tests. Bulk samples of soil around each column were collected during excavation of cylinders and analysed for additional soil properties.

Soil columns for hydraulic conductivity tests were saturated from the bottom for three days or more. A soft PVC mesh was provided at the bottom to prevent soil losses. The saturated hydraulic conductivity was determined under constant pressure head. No water flow was measured in some columns, and in others K_{sat} was significantly smaller than the unsaturated flow rate adjusted in the leaching tests. It appears that flow paths closed during saturation of samples due to processes such as swelling of clays, internal erosion or reduced structural stability resulting in very small K_{sat} values. These observations raise fundamental questions about the validity of the methodology used for determining K_{sat} and also indicate that the values obtained in this study were unreliable and unsuitable for statistical analysis or prediction efforts. Therefore, K_{sat} values were not considered any further in this study.

Bulk soil samples were utilised for determining the particle size distributions and total organic carbon (OC). A combined sieving and sedimentation method was used for particle size distributions. The soil suspension, after destroying organic matter with H_2O_2 and cementing

agents with HCl, was passed through graded sieves down to a particle diameter of 0.2 mm. Deflocculation was carried out and the method of sedimentation was followed to separate and classify finer particles according to the following limits: clay < 2 μm , silt 2–63 μm , sand 63–2000 μm . Organic carbon was determined directly by a combined dry-ashing coulometric method.

Bulk density and water content of soils of individual columns were measured after termination of leaching tests. The dry weight of soil of each column was determined by drying the samples at 105°C. Values obtained were divided by the volume of the column (V) to derive the bulk density (ρ_b) of the soil. The volumetric water content of the soil at time of sampling, Θ_f , was determined from the gravimetric water content (Θ_g) of the field fresh soil and ρ_b assuming a water density of 1 g cm⁻³: $\Theta_f = \Theta_g \rho_b$.

LEACHING EXPERIMENTS

The set-up for leaching tests was adapted from Rambow and Lennartz (1993). The apparatus (Fig. 1) induced unsaturated water flow conditions by applying a suction at the lower end of the samples, while the soil surface was at atmospheric pressure. Suction was conducted into the soil through the lower boundary that was made of a porous glass plate covered with an inert Nylon membrane. The leachate was withdrawn through the suction port via a vacuum lock operated by three magnetic valves. The lock allowed sampling of leachate without severe changes in the adjusted vacuum level. Four hypodermic needles formed the sprinkler unit which was used for applying the standardised bromide-free transport solution having ionic composition similar to that of naturally occurring rain water. A sprinkler supply from a Mariotte vessel was arranged by gravity, while irrigation was driven by magnetic valves. Due to small differences either in hose length from the bottle to each sprinkler or to differences in the conductivity of the sprinkler needles, irrigation amounts differed between samples. Adjustment of the irrigation amount of each individual column was not possible since all 24 sprinklers were connected to the same Mariotte bottle. Instead, effluent volumes were used to determine the flow rate of individual columns. Control of matrix suction was not possible during the experimental period, because samples were not equipped with tensiometers. However, the unsaturated hydraulic conductivity as a function of the matrix potential (K - Ψ -function) was known from large soil columns (15 cm in diameter and 15 cm in length) collected from the same sites (Meyer-Windel and Lennartz, 1995; Meyer-Windel *et al.*, 1996). The K - Ψ -functions were used to establish a uniform vertical soil water profile within the samples.

Twenty-four columns were mounted on the experimental set-up and the suction applied was -3 kPa for every batch. Prior to bromide tracer application, samples were adjusted to steady state water flow conditions at least for

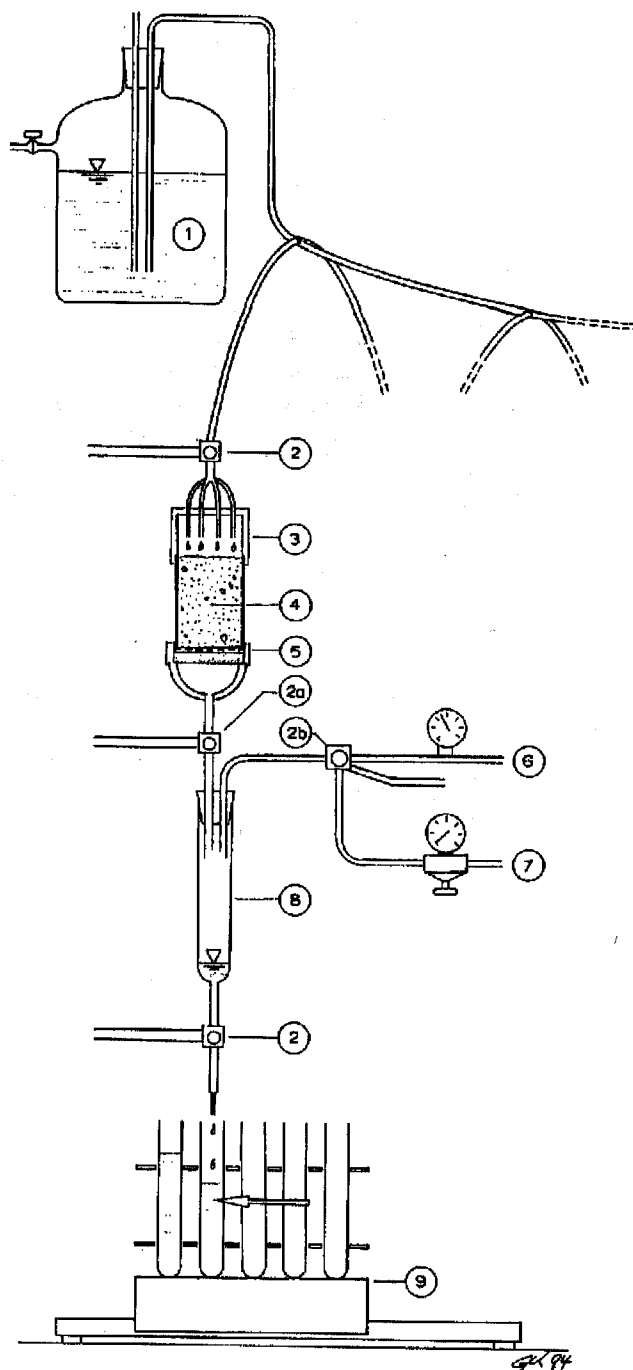


Fig. 1. Schematic diagram of the experimental set-up showing: (1) Mariotte vessel; (2) magnetic valve, powerless closed, (2a) powerless open, (2b) three way; (3) sprinkler; (4) soil column; (5) porous glass plate; (6) suction supply (7) pressure supply; (8) vacuum lock; (9) fraction sampler.

48 hours with a Darcy flux of 0.8 cm d⁻¹. After equilibration of steady state flow, a short bromide (KBr) pulse of 1 mL was applied in two equal parts. Bromide concentration was 960 mg L⁻¹ which resulted in a bromide mass of 0.960 mg for each column. Automatic sampling of leachate at 4 hour intervals was initiated simultaneously with the start

of tracer application. Sampling intervals corresponded to approx. 1/25 pore volume. The refined sampling resolution was chosen to ensure detection of preferential solute leaching situations. Columns were weighed immediately after the leaching tests and were oven dried for determination of water content. The leaching test failed in one column from each site due to technical problems; further analysis was therefore confined to 23 samples for site A and 35 samples for site B.

The experimental set-up was designed to treat a large number of samples simultaneously rather than to achieve a very high level of accuracy of water flux in individual columns. Nevertheless, the mean Darcy flux (\bar{q}) and the mean volumetric water content of the samples ($\bar{\Theta}_s$) of both sites were comparable ($\bar{q} = 0.81$ and 0.76 cm d^{-1} , $\bar{\Theta}_s = 0.33$ and $0.35 \text{ cm}^3 \text{ cm}^{-3}$ for site A and B respectively). The coefficient of variation (CV) among Darcy fluxes of site A columns as well as water contents at both sites were less than 10%. A larger CV (17%) for the Darcy flux of site B may be attributed to the fact that displacement experiments at site B were conducted in two batches of 24 and 12 columns each. Although the experimental settings were kept constant during the two batches of site B columns, it was observed that the difference between batches introduced additional variability. The CV for Darcy fluxes of columns of individual batches, however, continued to be less than 10%.

EVALUATION OF BREAKTHROUGH CURVES (BTCs)

The movement of bromide through undisturbed soil columns was assumed to be described adequately by the classical one dimensional convection-dispersion equation, CDE (Nielsen and Biggar, 1962)

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (1)$$

where c is the solute concentration (M L^{-3}), t is the time (T), x is the spatial coordinate in flow direction (L) and v is the pore-water velocity (L T^{-1}). The parameters gov-

erning equilibrium transport in equation (1) are the hydrodynamic dispersion coefficient, D (L T^{-2}) and the

dimensionless retardation factor, $\left(R = 1 + \frac{\rho_b K_D}{\Theta} \right)$ where

ρ_b is the soil bulk density (M L^{-3}), K_D is the linear adsorption coefficient ($\text{L}^3 \text{ M}^{-1}$) and Θ is the volumetric soil water content ($\text{L}^3 \text{ L}^{-3}$).

In its mechanistic sense the retardation factor, R , accounts for adsorption of reactive solutes ($K_D > 0$), shifting the response curve of a solute pulse to the right on the time axis. For non-sorbing solutes, like bromide ($K_D = 0$), R by definition should be equal to unity. However, R was found to be smaller than 1 in many studies involving non-reactive tracers (Gaudet *et al.*, 1977; Schulin *et al.*, 1987; Veeh *et al.*, 1994) indicating negative adsorption ($K_D < 0$). The latter phenomenon could be assigned either to anion exclusion (Schulin *et al.*, 1987) or to a reduction in flow cross sectional area caused by stagnant water regions not participating in solute transport (Gaudet *et al.*, 1977; Seyfried and Rao, 1987; Lennartz and Meyer-Windel, 1995). Anion exclusion volumina resulting from negatively charged clay surfaces were calculated according to Veeh *et al.* (1994). Based on average values of $1.5 \text{ m}^2/\text{kg}$ for clay surface area and $0.5 \times 10^{-9} \text{ m}$ for double layer thickness, and using the average bulk density of all samples of a site (Table 1) as well as the average water content of the steady state transport experiments ($\bar{\Theta}_s$), anion exclusion volumina of 3.6% and 3.7% of the water content were calculated for site A and B respectively.

Immobile soil-water was likely to occur under the chosen flow (unsaturated) and soil (undisturbed) conditions. Stagnant water phases lead, for pulse type application of non-sorbing solutes, to BTCs with a concentration apex before one pore-volume of effluent. To obtain reasonable fits with the simple CDE and measured BTCs that are shifted to the left on the time axis, either R or v needs to be varied during the fitting process. The retardation factor in its mechanistic sense reflects the sorption of a reactive chemical onto the soil and was used in this study to

Table 1. Statistical characteristics of soil properties from site A ($n=24$) and site B ($n=36$): Estimates of Mean, standard deviation (SD), coefficient of variation (CV in %) and calculated value of the Kolmogorov-Smirnov normality test (D).

Property	Mean	SD	CV	D	Mean	SD	CV	D
	Site A				Site B			
Θ_f ($\text{cm}^3 \text{ cm}^{-3}$)	0.30	0.04	12	0.084†	0.29	0.07	23	0.190†
Sand (%)	62.1	15.3	25	0.117†	54.3	9.83	18	0.138†
Silt (%)	25.7	10.7	42	0.089†	36.2	13.6	38	0.185†
Clay (%)	10.3	5.1	49	0.129†	10.9	4.82	44	0.129†
OC (g kg^{-1})	1.52	0.34	22	0.175†	4.58	2.0	44	0.203†
ρ_b (g cm^{-3})	1.53	0.07	4.6	0.114†	1.58	0.18	11	0.130†

† Null hypothesis is not rejected at the 0.15 level of significance (p).

include the anion exclusion phenomenon. Hence, v in addition to D were allowed to vary during the fitting procedure to account for immobile water. Optimised (v_{fit}) and measured ($v_{measured}$) values allowed the calculation of a solute mobility index (MI):

$$MI = \frac{v_{measured}}{v_{fit}} \quad (2)$$

with $v_{measured} = q/\Theta_m + \Theta_{im}$ and $v_{fit} = q/\Theta_m$.

The mobility index (MI) decreases as the amount of immobile water increases. If all the soil water is involved in the flow process MI becomes 1.

The dispersion coefficient, D , in a general sense accounts for several mechanisms contributing to overall solute spreading such as non-uniform intra- and inter-pore water velocity distributions, the tortuous nature of the pore-system and diffusion. When immobile water regions are present in the soil system, additional spreading due to diffusive solute transport into and out of the stagnant water regions is also lumped into the dispersion coefficient D . In such a case it is impossible to distinguish quantitatively between the individual spreading processes from the optimised parameter value. The effect of non-equilibrium processes caused by water regions of different mobility on solute transport, however, could be studied using models (Coats and Smith, 1964, van Genuchten and Wierenga, 1976) more complicated than the simple CDE. But a more complex approach like the two region model introduces additional parameters that are in general not determinable independently. When these parameters are obtained by simultaneous optimisation they describe the shape of the experimental BTC but they do not provide mechanistic information or physical insight into the transport process (Koch and Flühler, 1993). Consequently, the simple CDE (Equation 1) was chosen for evaluation of the data using computed D - and MI -values for the characterisation of the individual BTCs.

The parameters, v and D , of the (one dimensional) CDE can be determined from the experimental BTCs using graphical methods or curve fitting procedures (van Genuchten and Wierenga, 1986; Yamaguchi *et al.*, 1989) or by the method of statistical moments (Leij and Dane, 1991; Kamra *et al.*, 1996). Values of v and D were derived using the non-linear least square inversion program CXTFIT (Parker and van Genuchten, 1984) in which the parameter values are varied to best describe the experimental BTCs. Regarding anion exclusion as a negative-adsorption process, R was set fixed to 0.96 for BTCs of both sites during the fitting. The tracer pulse length was also kept constant during the fitting procedure after correction for mass recovery.

Results and Discussion

SOIL PROPERTIES

Statistical evaluation of soil parameters of two experimental sites revealed frequency distributions which were tested for normality using Kolmogorov-Smirnov criterion. The null (normal) hypothesis was not rejected at 0.15 level of significance. Organic carbon (OC) content at site B failed to satisfy the normality criterion; all other parameters (sand, silt, clay content, ρ_b , Θ_f) exhibited a normal frequency distribution. This result is in accordance with findings from Cambardella *et al.* (1994). The frequency distributions of field moisture content (Θ_f), soil bulk density (ρ_b) and texture parameters of both sites had coefficients of variation (CV) less than 50% (Table 1).

The mean values of Θ_f , ρ_b and clay content at two sites were comparable; site B, however, had 10% more silt and three times more organic carbon than at site A (Table 1). Increased organic carbon resulted perhaps from occasional water-logging and subsequent reduced biological activity at site B, while its subangular soil structure had some correlation with the silt content. Coefficients of variation in respect of Θ_f , ρ_b and OC at site B were also almost double than at site A. These aspects seem to have important bearing on the variability in solute transport characteristics including inducement of preferential flow at site B vis à vis site A as discussed in forthcoming sections.

BROMIDE BREAKTHROUGH BEHAVIOUR AND MASS RECOVERY

The breakthrough curves (BTCs) resulting from leaching experiments of the two sites could be divided into two groups whose representative forms are shown in Figure 2. In type I BTCs, the maximum concentration (ranging from 12 to 35 mg L⁻¹) occurred between 0.4 and 0.8 pore volumes of effluent followed by a more or less pronounced tailing. The shape of type II BTCs was characterised by preferential flow features like extreme early breakthrough (with peak concentrations of more than 35 mg L⁻¹) at about 0.2 pore volumes, followed by a steep decrease in concentrations and a long tail at larger pore volumes. Only one BTC of site A, because of irregular features like double peak behaviour, did not fit in either shape group. The double peak behaviour was also treated as a preferential flow feature and included in type II curves. This resulted in the identification of 6 preferential flow columns (PFCs, type II BTCs) for site A and 8 for site B. The remaining 44 of the total 58 curves had type I shapes.

The occurrence of concentration maxima of non-reactive tracers between 0.4 and 0.8 pore volumes (type I BTCs) reflects the presence of immobile water between 60% and 20% which was likely to occur under the chosen flow conditions. In this study, therefore, type I BTCs present the classical solute movement behaviour expected under unsaturated steady state water flow conditions. The

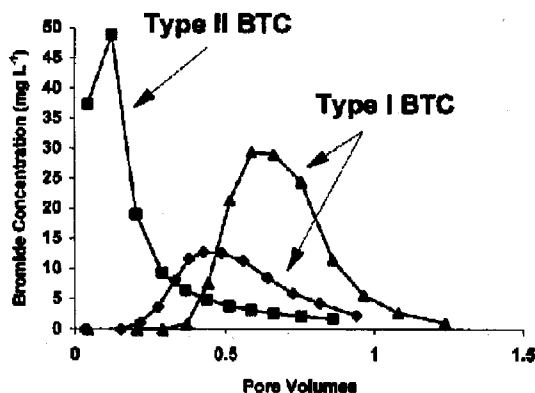


Fig. 2. Observed bromide breakthrough curves: type I = classical (non-preferential), type II = preferential breakthrough behaviour.

type II (preferential flow) BTCs document stagnant water phases in the soil equally well, although the volumes are greater (> 65%). Type II BTCs were not likely to occur since the potential macropores, fissures or column-side-wall fractures were expected to get desaturated and not to contribute to flow under these conditions. The early breakthrough in type II columns is thought to be caused by flow through the soil matrix, rather than along macro-pore walls, for which a kind of fingering flow (Kung, 1990) was the governing transport phenomenon. Local particle arrangement or water repellent structures seem to be responsible for significant reduction in the cross-sectional area involved in water flow. Preferential finger flow through the soil matrix may be considered as an extreme case of the mobile-immobile concept.

There was wide variability in the leached fraction of applied bromide mass in different columns though the mean leached mass was comparable (86% and 84%) at the two sites. The range (68–96%) and associated CV (8.6%) of recovered bromide in different columns of site A was relatively small as compared to the range (39–114%) and CV (23%) observed amongst columns of site B. Further, the solute behaviour in terms of recovered mass differed in preferential flow columns (PFCs) of both sites. At site B, less bromide eluted from PFCs than from normal type I columns and it was estimated that 8 PFCs contributed to 51% of the total variance of recovered mass at site B. The range of mass recovery for columns of site A was essentially the same for the two types of BTCs.

Differences in mass recovery from type II BTCs between sites are probably influenced by soil structure. Samples of site A showed a crumbed structure while the peds at site B had subangular shape. The average diameter of aggregates from site B as determined from visual inspection (2–4 mm) was two to three fold larger than that from site A aggregates (1–2 mm). It is assumed that bromide leaching continued from the aggregates via diffusion, even after the elution of the main portion of bromide mass from the preferential flow region. Larger diffusion path

length of the bigger aggregates of site B led to less bromide transport from the intra aggregate to the preferential pore space during the course of the study. Further, a slower diffusion rate was probably faked by a temporal bi-directional concentration gradient that directed transport towards the preferential pathways as well as towards the centre of the aggregates. In contrast, diffusion of bromide in columns of site A occurred in a direction away from the ped centre after the main peak was leached from the preferential region. As a consequence, bromide leaching was less efficient in columns of site B.

SOLUTE TRANSPORT PARAMETERS

The least square fitting procedure, CXTFIT, yielded in about 75% of the model runs (43 out of 58) a fitting criterion (r^2) above 0.95. A typical fit of such curves is shown in Figure 3a. In 11 (both type I and II) curves, r^2 ranged between 0.80 and 0.95. The goodness of fit was lower in these BTCs either because of irregular shapes of some of the type I BTCs or because of inadequacy of the simple CDE model to exactly describe the long tail of type II BTCs. Despite its failure to reproduce the tail of type II BTCs, the CDE model successfully matched the concentration apex as illustrated for one such type II BTC in Figure 3b. Consequently, v_{fit} -values and the corresponding MI-values were considered to be a reliable measure describing the position of the concentration maximum on the dimensionless time axis even under preferential flow conditions. Three model fits had r^2 -values between 0.6 and 0.8, but the calculated v_{fit} and D values were unambiguous, as the same values were obtained irrespective of the initial guess in the fitting procedure. One double peak BTC (Fig. 3c) could not be described by the CDE (r^2 less than 0.6) and its parameters were not included in succeeding analyses.

Examination of MI-values confirmed conclusions drawn earlier from visual inspection of the BTCs. At site B, 8 columns had MI-values between 0.11 and 0.21 indicating pronounced preferential flow. For the remaining 27 columns, MI varied from 0.55 to 0.82. At site A, 5 columns had MI-values less than 0.35 and these were classified as 'preferential'. Small MI-values of PFCs invariably had large D-values to reflect the long tail of these BTCs. Frequency distributions of MI- and D-values from both sites (Figure 4) were not normal and even their log-transformation did not lead to normal distribution under the Kolmogorov-Smirnov normality test criterion. The distribution of MI-values of site A was negatively skewed and conversely the distribution of the D-values had an asymmetrical tail extending towards the right. At site B, the frequency distributions of both MI and D were bimodal, indicating two distinct sample populations with respect to transport parameters.

Descriptive statistics for MI- and D-values for combined (type I and type II) and type I columns alone are

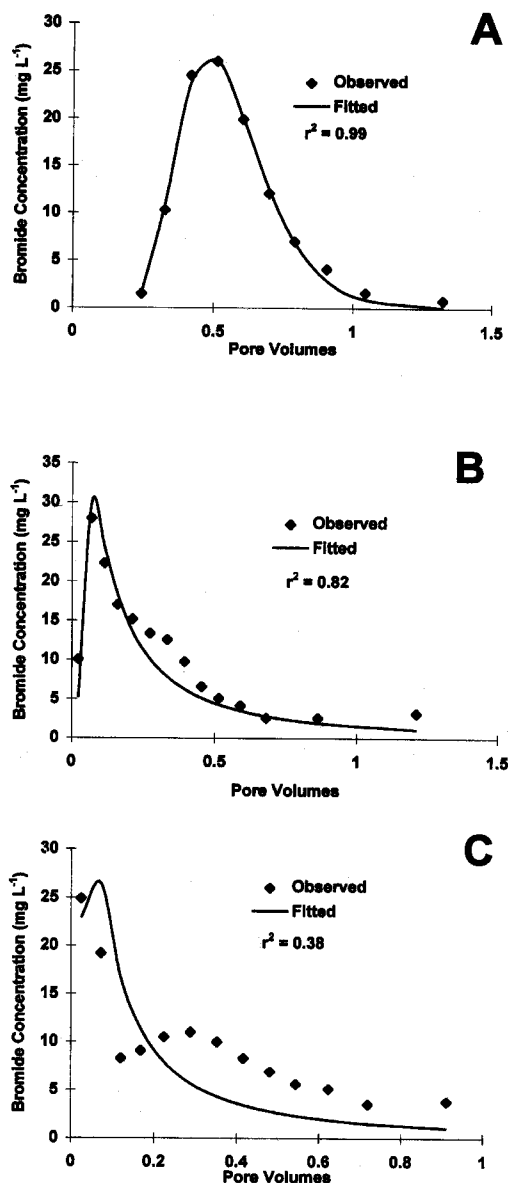


Fig. 3. Observed and optimised (CDE) breakthrough curves for (A) classical, (B) preferential and (C) bimodal transport situations.

provided in Table 2. The arithmetic means of MI-values of both sites were comparable, but the mean value of dispersion coefficient, D , of site A was more than three times larger than that of site B. Exclusion of PFCs from the analysis reduced the mean values of D of both sites, but differences remained. The larger mean D -values as well as the resulting dispersion length ($\lambda = D/x$) (Table 2) of site A can be assigned to the structure and resulting differences in pore geometry of both sites. It has been stated earlier that site A samples were dominated by small sized crumb aggregates. A larger number of small peds obviously increased dispersivity compared to bigger aggregates of site B samples. The CV for dispersion coefficients of both sites was about 100% when all samples were consid-

ered. For non-preferential flow (type I) columns, the CV for dispersion coefficients decreased to 80% for site A and 34% for site B, indicating a higher contribution of PFCs at site B to the overall variability of dispersion coefficient.

SPATIAL DISTRIBUTION OF BROMIDE TRANSPORT

Solute movement in heterogeneous flows could be quantified in terms of either resident concentrations (c) defined as the solute mass per unit volume, or the mass flux (s) which refers to solute mass crossing a given surface in unit time (Sassner *et al.*, 1994). The latter quantity is more relevant in assessing the contaminant discharge at a specific depth (for example, the groundwater table) and was used in this study to illustrate the time evolution of mass flux of bromide at a 10 cm depth plane in the field. Because 10 cm depth is too small for field scale evaluation, the basic thrust was to propose a methodology for evaluating the basic differences in leaching characteristics of preferential and non-preferential flow regions in the field rather than to provide any measures of relevant quantities. Mass flux of bromide per unit cross sectional area, s , was calculated from water flux density, q , and the bromide concentration, c , of individual columns as $s = c q$. The mass flux was normalised with the surface density (mass per unit cross-sectional area) of applied solute.

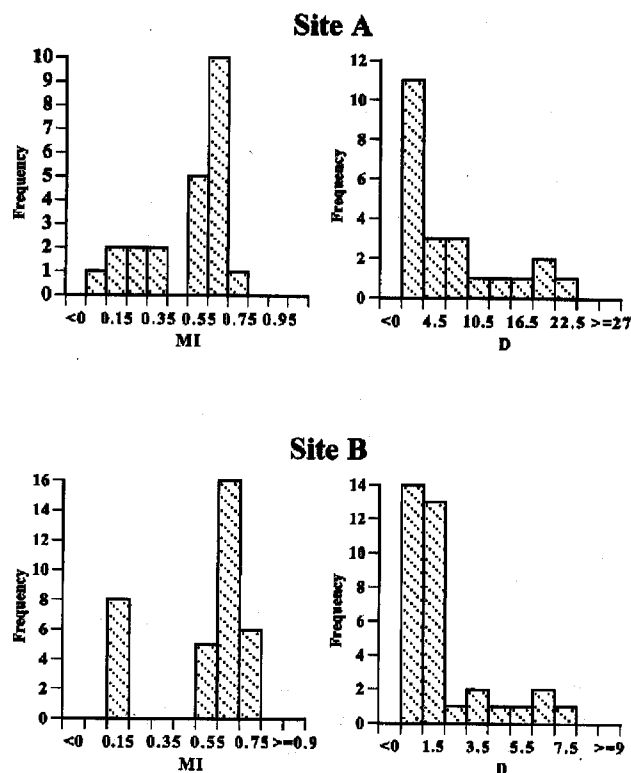


Fig. 4. Frequency distributions of the mobility index (MI) and the dispersion coefficient (D , $\text{cm}^2 \text{d}^{-1}$) of (a) site A and (b) site B.

Table 2. Descriptive statistics for the mobility index (MI), dispersion coefficient (D) and dispersivity (λ) of two sites: Estimates of Mean, standard deviation (SD) and coefficient of variation (CV in %).

	MI (-)			D (cm ² d ⁻¹)			λ (cm)		
	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
<i>Site A</i>									
Total Samples (n=22)	0.53	0.17	32	6.24	6.23	100	2.67	2.9	107
Type I (non-preferential flow columns, n=17)	0.61	0.07	12	3.87	3.09	80	1.52	1.27	84
<i>Site B</i>									
Total Samples (n=35)	0.53	0.23	43	1.96	1.90	97	1.05	1.17	111
Type I (non-preferential flow columns, n=27)	0.65	0.07	11	1.03	0.35	34	0.44	0.16	37

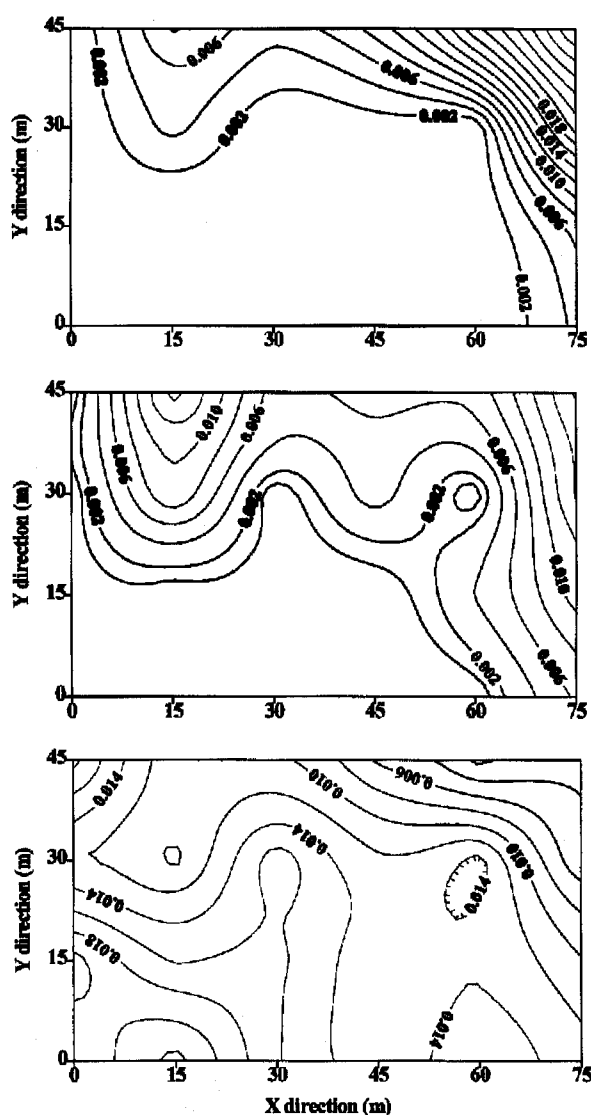


Fig. 5. Contour maps of bromide mass flux (normalised, h^{-1}) at 10 cm depth plane for site A at 0.1 (top) 0.2 (middle) and 0.5 (bottom) pore volumes of effluent.

The contour lines of normalised flux (h^{-1}) for the two sites are plotted for certain dimensionless time steps in Figures 5 and 6. It is observed that only preferential flow, clustered in a small section of area at both sites, contributed to the mass flux of bromide during initial stages of breakthrough. The peak of the mass flux in preferential flow area was reached apparently at about 0.1 pore volumes. This early flow occurred in a larger fraction of the total area at site A but had comparable values of peak mass flux with site B. At 0.2 pore volumes, breakthrough was initiated in only a small additional area at site A but the magnitude of mass flux in preferential flow area decreased at both sites. At this time, the preferential peak of mass flux was almost over while the expected 'classical' peak had not yet started. During later stages at 0.5 pore volumes, which corresponded roughly to the mean MI of the two sites (Table 2), the whole surface area contributed to bromide mass flux. However, the largest values occurred where there was no mass flux during earlier stages while the elution of bromide from preferential flow areas was less important. It is interesting to note that the observable difference in maximum mass fluxes in preferential and non-preferential areas, in particular for site B, was limited only to its time of occurrence rather than its magnitude.

SOLUTE MOVEMENT AND RELATION TO OTHER SOIL PROPERTIES

Linear cross-correlations were calculated between selected soil properties and calculated MI- and D-values of all (combined type I and II), non-preferential (type I) and preferential (type II) columns. The matrix of correlation coefficients for different types of columns of the two sites is presented in Table 3. The number of preferential columns was small, and consequently no firm conclusions are intended for these columns even for relations with apparently significant levels of correlation coefficients. Further, significance of correlation is not marked in Table

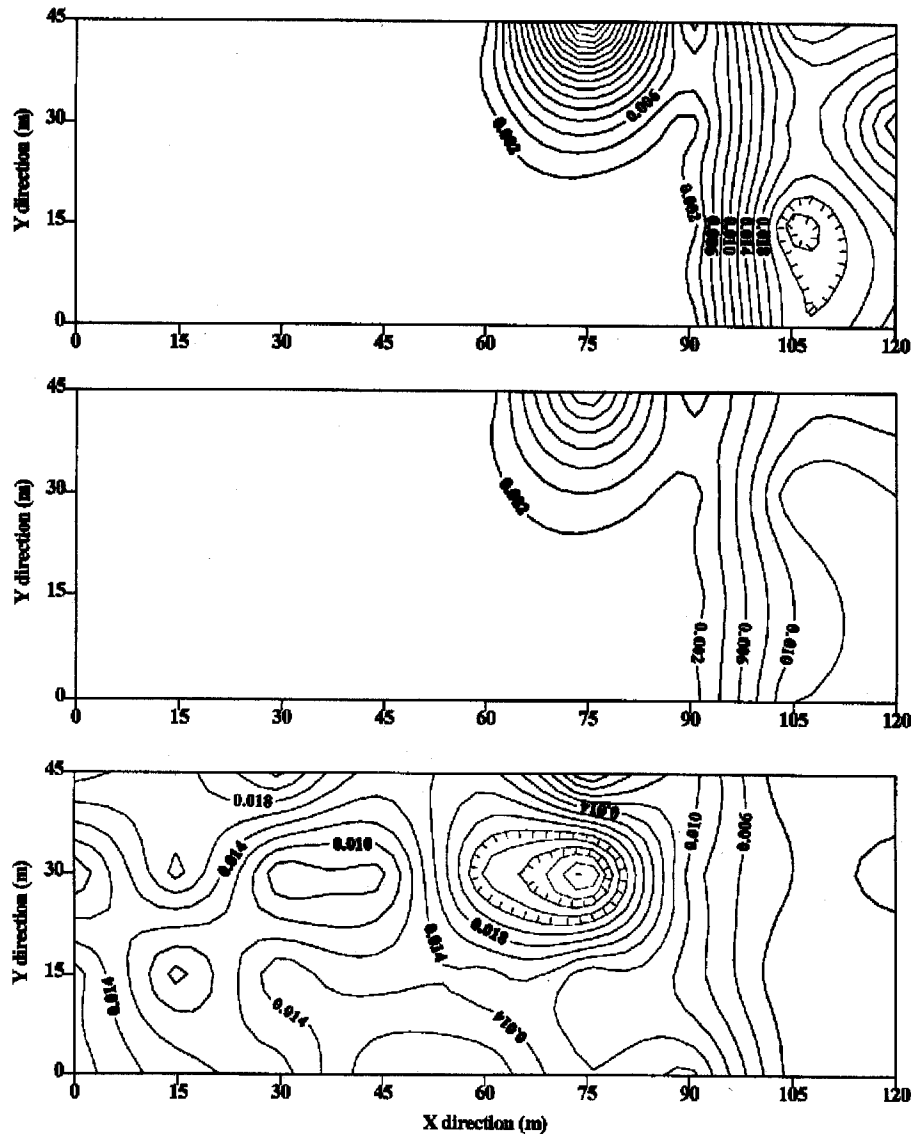


Fig. 6. Contour maps of bromide mass flux (normalised, h^{-1}) at 10 cm depth plane for site B at 0.1 (top), 0.2 (middle) and 0.5 (bottom) pore volumes of effluent.

3 for analyses involving all (both type I and type II) columns since frequency distribution of MI- and D-values did not satisfy the normality criterion.

For combined columns, the mobility index (MI) and the dispersion index (D) had relatively larger correlation coefficients (r) with the volumetric soil water content at time of sampling, Θ_f , and clay content at site A and with Θ_f and organic carbon content at site B. Still higher correlations between transport parameters and these properties for combined columns seem to be hampered by the fact that the frequency distribution of these properties were continuous and normal (except for OC at B) while of MI and D were formed by either two populations (site B) or were extremely skewed (site A).

The volumetric soil water content in the field at time of

sampling, Θ_f , was treated in this study to represent a simple form of the hydraulic behaviour of the soil. Negative correlations between MI and Θ_f indicate faster solute mobility in columns that originated from sampling locations with a greater water holding capacity at a given precipitation scenario than other sampling spots. Unfortunately, no significant correlation between MI and Θ_f was observed when either type I or type II BTCs were considered separately in the regression analysis. At a certain threshold of Θ_f solute transport turned from advective-dispersive to preferential. Though the CV of Θ_f at both sites was small compared to other soil properties (Table 1), Θ_f seems to be an important parameter influencing solute mobility. A preliminary indication from this study is that Θ_f is a highly sensitive parameter with respect

Table 3. Estimates of linear cross correlations coefficients (r) among mobility index (MI), dispersion coefficient (D) and selected soil properties. * marked correlations are significant at $p < 0.05$. Significance was not indicated when all samples were used in correlation analyses since frequency distribution of MI and D did not fulfil normality criterion.

	Θ_f	Sand	Silt	Clay	OC
Site A					
Total samples (type I and type II; n=22)					
MI	-0.64	0.55	-0.54	-0.67	-0.42
D	0.65	-0.61	0.56	0.73	0.35
Type I (non-preferential flow columns; n=17)					
MI	-0.32	-0.04	0.09	-0.22	-0.06
D	0.57*	-0.31	0.42	0.38	0.16
Type II (preferential flow columns; n=5)					
MI	-0.71	-0.18	-0.03	0.09	-0.03
D	0.39	-0.49	0.05	0.86	-0.33
Site B					
Total samples (type I and type II; n=35)					
MI	-0.75	0.55	-0.15	-0.35	-0.64
D	0.72	-0.37	0.04	0.47	0.62
Type I (non-preferential flow columns; n=27)					
MI	0.24	0.65*	-0.19	0.15	-0.25
D	0.31	-0.37	0.18	-0.10	0.30
Type II (preferential flow columns; n=8)					
MI	-0.68	-0.02	-0.09	0.20	-0.15
D	-0.42	0.30	-0.49	0.52	0.11

to the risk for preferential transport. Specific studies need to be undertaken to explore this aspect for different soils under varying flow regimes. For type I curves, only D of site A had a significant correlation to Θ_f . For type II curves, D had no correlations with Θ_f at both sites.

Both solute transport parameters of site A were related to the clay content of sampling locations. At site B, only the sand fraction seemed to influence solute movement in NPFCs, but organic carbon content was more important when all samples were considered. The role of organic matter on preferential solute transport has been documented. Organic matter causes water repellency resulting in establishment of preferred flow zones which persist over several infiltration cycles (Buchter *et al.*, 1995).

Multiple regression analysis was carried out among solute transport parameters and independently determined soil properties. Since no combination of parameters markedly improved regression criterion compared to linear regression, results are not presented.

Summary and Conclusions

Bromide displacement tests were conducted in small undisturbed soil columns under unsaturated steady state flow

conditions to derive frequency distribution of solute transport parameters for two field plots. Columns were collected at a relatively coarse grid of 15 m at both sites with a view to cover small field size areas with a limited number of samples. The soils at both sites differed in texture and structure. Measured bromide breakthrough curves (BTCs; 23 for site A, 35 for site B) were analysed with the convective-dispersive equation. The optimised pore water velocity values were used to calculate a solute mobility index (MI). Columns exhibiting preferential flow features like early breakthrough and extensive tailing were identified and their contribution to solute distribution patterns in the field was evaluated. Correlations were calculated between solute transport parameters of preferential and non-preferential flow columns and independently determined soil properties. Following salient observations and conclusions seem to emerge as an outcome of this study:

Despite a relatively small Darcy flux of (0.8 cm d^{-1}), and unsaturated water flow conditions, 26% of samples at site A and 23% at site B exhibited preferential transport features. A threshold of the mobility index MI of $\text{MI} < 0.35$ was used as a criterion for the occurrence of preferential solute movement. The results clearly demonstrate that preferential solute transport is not confined to 'worst case scenarios' related to water saturated conditions, rare storm events or to heavy soils but could occur in any type of soil or flow regime. The conclusions from the given results are limited to 10 cm soil depth though several field studies employing various techniques have demonstrated that the problem continues over larger travel distances (Kladivko *et al.*, 1991, Roth *et al.*, 1991, Flury *et al.*, 1995).

The equilibrium based CDE adequately described measured bromide BTCs except of one which exhibited double peak behaviour. In particular, the CDE model successfully matched the concentration apices of all BTCs including those with preferential flow features. Frequency distributions of computed MI- and D-values were either bimodal indicating the presence of two distinct populations or were heavily skewed. Log transformation of these values did not yield a normal distribution for any breakthrough parameter. For site A columns, D-values were three times larger (*vis-a-vis* site B columns) which was possibly due to differences in the structure and resulting pore geometries of the two soils.

A 'field scale' view of the bromide breakthrough behaviour was obtained by plotting contour lines of bromide mass flux of individual columns over the experimental area. The methodology was found suitable to present the evolution of the mass flux of bromide eluting at 10 cm soil depth in the whole field. Soil surface areas contributing to preferential flow were clustered at both sites. No other measured soil property showed similar behaviour.

Correlation analysis among solute transport parameters and independently measured soil properties revealed that soil texture, mainly clay content, was related to the preferential flow phenomenon. Since clay content influences

the soil water capacity, solute mobility was also related to the volumetric soil water content at the time of sampling. The field soil water content, a simple parameter reflecting soil hydraulic properties at the sampling location seems to be a good measure for assessing the preferential flow risk in a particular soil. Even a small variability in the moisture content in the field is likely to enhance the probability for occurrence of preferential transport situations. The mobility of bromide was also related to the organic carbon content in one of the soils studied where organic carbon was high. However, it can be concluded from correlation analysis of individual preferential or non-preferential flow columns that prediction of classical and preferential solute movement, is not possible with empirical equations based on parameters measured in this study. Future experimental work should concentrate on relating more integrative parameters such as the infiltration rate or the soil hydraulic functions to preferential solute movement.

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